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Reactive Systems. Variation of Initial Energy Distribution

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Single Collision Gas-Surface Vibrational Energy Transfer

in Reactive Systems. Variation of Initial Energy Distribution[*]

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Abstract

The initial vibrational energy distribution of molecules that collide with a hot surface has been varied. The effect of the variation on the collisional reaction probability (P_c) has been studied under single collision conditions. These experiments provide a more sensitive test of the relative suitability of various analytical forms for the collisional transition probability matrix, $\underset{\sim}{P}$, than has been achieved previously in earlier VEM experiments. The reaction system is the isomerization of cyclobutene to 1,3 butadiene. A seasoned fused quartz surface was used over the temperature range $T_r = 600\ K - 900\ K$. Variation of the initial vibrational energy population vector of cyclobutene molecules was made by change of their initial temperature T_c in the range $273\ K - 620\ K$. The experimental collisional efficiency, β_1, declined from 0.31 to 0.013 over the combination temperature ranges $T_r, T_c = 600,500$ to 900,273. Stochastic models of the vibrational transition probability were fitted to the data and provided values for the average amount of energy ($<\Delta E'>_{E_0}$) transferred from the hot molecules in a down transition from the threshold energy level E_0; Gaussian or Boltzmann Exponential forms of $\underset{\sim}{P}$ prove to be the most suitable to fit the data. Calculated values, $<\Delta E'>_{E_0}$ on the basis of a Gaussian function model for $\underset{\sim}{P}$ declined from 5600 cm^{-1} to 3700 cm^{-1} with increase in the surface temperature from 600 K to 900 K.

INTRODUCTION

Because of the interest in gas-surface interaction, energy accommodation at a surface continues to be actively studied both experimentally and theoretically.[1-5] Very little work has been done on collisional transfer of vibrational energy between a surface and polyatomic molecules at the level of vibrational excitation corresponding to reaction in non-catalytic processes. A technique for this purpose called the Variable Encounter Method (VEM),[4] has been reported recently. VEM provides a measure of vibrational energy transfer between initially cold molecules and a hot surface: gas molecules describe a random walk along an energy coordinate until they reach an absorbing level — the critical reaction threshold E_0 characteristic of the homogeneous gas reaction. Such relaxation of non-equilibrium vibrational energy distributions was described theoretically a number of years ago by Rubin and Shuler,[6] Kim,[7] and by Widom.[8]

In the previous VEM work,[4,9-12] gas molecules were thermally equilibrated in a reservoir flask at some low temperature and then entered a hot reactor in which they experienced a known (and experimentally variable) average number, m, of sequential collisions with the surface before leaving the reactor and re-equilibrating to their initial low temperature; m was varied between 2 and 30. A fraction of the molecules are excited above the reaction threshold energy during the series of wall collisions and experience homogeneous unimolecular reaction. The nature of the collisional relaxation of the vibrational energy transients may be deduced from the experimental reaction rate. Systems involving surface catalysis have been avoided.

Recently, single collision measurements (m=1) by the VEM technique have been described.[13] In the present paper we have applied the single collision condition to the study of the effect of variation of the initial vibrational energy on the single collision reaction (transition) probability. The surface

is a seasoned fused quartz finger. Although such a surface is not well defined, it is the conventional experimental surface of thermal unimolecular kinetics. Unlike low-energy non-reactive accommodation studies that involve translational, rotational and vibrational degrees of freedom, vibrational energy is the main contributor to the reaction probability for reacting systems that involve small or zero centrifugal energy barrier effects; in such case, rotational energy plays little role.[14] This is the case here for the study of cyclobutene unimolecular isomerization to 1,3-butadiene. The reaction has a low activation energy, 32.4 kcal mole^{-1}, and proceeds with no evidence for surface catalysis.[10,11,13]

The vibrational energy population vector of molecules after one collision, $\underset{\sim}{N}_1$, is given by $\underset{\sim}{N}_1 = \underset{\sim\sim}{PN}_C^{eq}$, where $\underset{\sim}{P}$ is a collisional transition probability matrix, and $\underset{\sim}{N}_C^{eq}$ is the initial vibrational energy population vector that corresponds to the thermal Boltzmann distribution at the low temperature of the gas reservoir wall. Since no comprehensive theory of gas-surface collisional interaction exists, at least for complex molecules on these surfaces, down-jump transition probabilities were constructed according to various assumed trial analytical models. Four models have been applied to the present interpretations; exponential (E), Gaussian (G), and Boltzmann distribution weighted exponential (BE) and Gaussian (BG) functions have been used in conventional thermal[15] and VEM[10,13] systems. Up-transition probabilities were constructed from the down-jump transitions, with use of detailed balance and completeness. Vibrational energy transfer above the reaction threshold, $E_i \rightarrow E_j$ ($E_j \geq E_o$), is the measured process of the reaction in a single collision reactive system. The transition probability matrix $\underset{\sim}{P}$ is a function of the reactor finger surface temperature. For simplicity, it was taken to be independent of the temperature of the reservoir wall and, hence, of variation of mean translational energy of the molecules and, therefore, of small variation of the residence

time of colliding molecules on the reactor surface.

Variation of the initial population vector by change of the wall temperature constrains the models of the collisional probability matrix that can reproduce the experimental reaction probability function and provides a more sensitive test of the aptness of the various trial functions than has been available hitherto by this technique.

EXPERIMENTAL

The cyclobutene (Columbia Chemicals, > 99.9%) showed no impurities on gas chromatographic analysis. The reaction system apparatus used here was similar to that of the previous single collision experiments (Fig.1 of ref 13). The reaction vessel consisted of a 3-ℓ spherical pyrex reservoir flask that was provided with an internally heated, central fused quartz finger. The flask and the quartz finger were heated independently. The heater control of the finger is described in the previous work. The wall temperature of the flask was controlled by an air oven consisting of a 30-cm cubic insulated box equipped with two plate heaters and an air-mixing stirrer; except that the lowest flask temperature (273 K) was attained by cooling the flask in an ice bath. Temperature measurements were made with four chromel-alumel thermo-couples cemented to the outside of the reservoir flask. The surface tempera-ture of the reactor finger was varied from 600 K to 900 K, while the wall temperature of the flask reservoir was varied from 273 K to 600 K. Temperature deviation of the finger surface was a maximum of $\pm$ 5°K at 900 K, and that of the flask wall was $\pm$ 10°K at 600 K. Before kinetic measurements were made, the reactive surface of fused quartz was "seasoned" at the highest temperature and the seasoning was maintained by exposure for a few hours to cyclobutene at a pressure of $\sim$ 5×10^{-3} torr prior to each run.

The system was run in both static and flow modes in the pressure region between 10^{-4} and 10^{-3} torr, usually $\sim$ 2×10^{-4} torr. For the static mode, the reactor was pumped to < 10^{-6} torr before substrate was introduced. The reaction gas was transferred for analysis after a predetermined run time. For the flow mode, the impedance of a variable exit valve was calibrated by pressure-drop measurements. Typical residence times were 10 to 40 sec. The run was

terminated by closing the variable flow valve after about 30 to 100 sec of reaction time. More detailed description of the flow analysis was given earlier.[13] Pressure measurements were made with an MKS Model 170 capacitance manometer.

Product analysis was performed by gas-liquid chromatography on a 5 ft x 3/16 in. squalane column on Chromosorb P at 0°C with FID detection.

RESULTS

Observed rate constants for cyclobutene isomerization to 1,3-butadiene were calculated from the product yield. The total observed rate constant k_t was a sum of reaction due to heating at the reactor finger, k_r, and at the reservoir wall, k_c, given by

$$k_t(T_r,T_c) = k_r(T_r,T_c) + k_c(T_c) ,$$

where T_r and T_c are the temperature of the finger surface and of the reservoir wall, respectively. k_c proves negligible for small T_c values. Independent measurements of the $k_c(T_c)$ were made under the experimental condition, $T_r = T_c$, with use of a minor area correction for the relative surface area of the reactor finger and the reservoir wall (1:13). The reaction rate constants k_t and k_c are shown in Fig. 1. The rate of k_c rises rapidly with an increase in T_c because of the larger area of the reservoir wall. Experimental measurements of k_r were rejected in the cases when correction for k_c amounted to $\gtrsim 50\%$ of the total rate k_t; these rejected values are marked with an X in Fig. 1. The reaction probability per collision, $P_c(T_r,T_c)$, was calculated from the finger surface reaction constant $k_r(T_r,T_c)$. Relative values of the reaction probability are plotted as a function of the T_c temperature in Fig. 2 on the basis of $P_c(T_r,273) = 1$. Error bars represent experimental uncertainty. As is reasonable, increase of T_c has greater effect when T_r is smaller. Experimental values of the reaction probability per collision are listed in Table 1. The experimental uncertainties in P_c are estimated to vary from $\sim 10\%$ at low T_c temperature to as much as 20% at high temperature. The collisional efficiency, β_1, defined as $\beta_1 = P_c(T_r,T_c)/P_c^{SC}(T_r)$ is also given in Table 1. The elements of $P_c^{SC}(T_r)$ are simply the Boltzmann distribution population vector for a unimolecular reaction in the low pressure regime. They were calculated with use of the vibrational frequency assignments of Elliott and Frey.[16]

DISCUSSIONS

The following experimental and theoretical simplifications in the present type of study which increase the power of the method should be noted. First, no knowledge of molecular collision cross-sections is involved. Second, if the reaction process is complete within the free flight time of the molecule when it leaves the surface, then the magnitude of the specific decomposition probabilities $k(E)$ do not enter. The reaction is in the unimolecular low pressure regime and neither a postulated activated complex structure nor RRKM calculations are required. This is the case here; decomposition under all conditions exceeds 99% of the activated molecules.

Variation of $P_c(T_r, T_c)$ with T_c is shown in Fig. 3 for each value of T_r studied. Several fits to the experimental data were made on the basis of various assumed analytical forms. The mathematical forms are exponential, E , gaussian, G , Boltzmann exponential, BE, and Boltzmann gaussian, BG. The corresponding forms of the probability, $P(\Delta E)$, of a <u>down</u> transition of energy, ΔE , are given by Eqs. (1) - (4).

$$P^E(\Delta E) = c_1 \exp(-\Delta E/\langle\Delta E\rangle) \tag{1}$$

$$P^G(\Delta E) = c_2 \exp(-(\Delta E - \Delta E_{mp})^2/2\sigma^2) \tag{2}$$

$$P^{BE}_{i \leftarrow j}(\Delta E) = c_3 B_i P^E(\Delta E) \tag{3}$$

$$P^{BG}_{i \leftarrow j}(\Delta E) = c_4 B_i P^G(\Delta E) \tag{4}$$

Here, $\langle\Delta E\rangle$, ΔE_{mp}, and σ are adjustable parameters, the c_i's are constants, and $B_i = g_i \exp(-E_i/RT_r)$ is a normalized Boltzmann distribution characteristic of the finger surface temperature, T_r, where g_i is the density of vibrational states at energy level E_i. The E and G forms of Eqs. (1) and (2) have been termed "flat" forms previously since the transition probabilities are independent of energy level. They are inadequate to describe near-strong collider

behavior since, as strong collider behavior is approached, the transition probability should approach the Boltzmann probability function, $P_{i \leftarrow j}(\Delta E) = B_i$. Hence, the Boltzmann weighted models of Eqs. (3) and (4) were also applied to the data. In earlier VEM studies ($m > 1$), the E model produced the best agreement with the experimental data of cyclobutane over the range of reaction surface temperatures from 749 K - 1126 K[9] and with the methylcyclopropane system from 800 K - 1130 K.[12] The G model was found to give the best overall fit to the data[4] for 1,1-cyclopropane-d_2;[4] while the BE model was used for the cyclobutene reactive system ($m=1$) over the lower temperature range[13] 400 K - 915 K, although the E and G models fit better at higher temperatures.[11]

Results of least squares fitting to the experimental P_c curves for each of the four analytical forms of $\underline{P}$ tested are also shown in Fig. 3; variation of $<\Delta E>$, or ΔE_{mp}, was the parameter of fit. The best fit values are listed in Table 2. We use and exhibit these average best-fit values rather than enumerating a multitude of individual best-fit values for each T_c for a given T_r. For the G and BG models, calculation was made with the standard deviation set at $\sigma = 0.7\ \Delta E_{mp}$, as in our earlier calculations. The calculated values of $<\Delta E'>_{E_0}$, the average amount of energy transferred in a <u>down</u> transition from the threshold energy level, E_0, are also given. Other quantities of interest are ΔE_{av}, ΔE_{av}^+. ΔE_{av} is defined as $\Delta E_{av} = \bar{E}_f - \bar{E}_c$, where $\bar{E}_c$ is the average energy of molecules at temperature T_c before collision and $\bar{E}_f$ is the average energy after collision. The other useful quantity ΔE_{av}^+ is the amount of average energy transferred above the critical threshold defined as $\Delta E_{av}^+ = [(\bar{E}_f)_{E_f > E_0} - E_0]$. They are listed with results of G and BE model calculations in Table 3.

The conventional vibrational energy accommodation coefficient, α, is defined as $\alpha = \Delta E_{av}/(\bar{E}_r - \bar{E}_c)$, where $\bar{E}_r$ is the average vibrational energy of molecules equilibrated at reactor temperature T_r; values are given in Table 3. Average vibrational energies of cyclobutene molecules for the various thermal equilibrium populations are given in Table 4.

The features of the experimental P_c curve in Fig. 3 are relatively flat lines at $T_c \lesssim 400$ K and a steeper rise at $T_c > 400$ K. The P_c curves calculated with both the G and BE models agree substantially with the data, with the former giving somewhat better fit. But the only model that can fit the inefficient flat behavior in P_c at low T_c is the E model. In general, however, both E and BG curves differ most from the bulk of the data and illustrate the extreme behavior of weak and strong collider behavior, respectively.

If one compares ΔE_{av} for G and BE models which are both fairly well fitted to the data, the relative values seem paradoxical: that for G is very big and that for BE very small, although both reproduce the experimental values of P_c and the general shape in Fig. 3. Again α is large for G and small for BE (Table 3). The explanation is to be found in Fig. 4, a typical plot. The plot of N_1^G follows N_{T_r} at low energies corresponding to high α^G values. However, above E_0 the N_1^G values drop relative to N_1^{BE} which never attain N_{T_r} but do not tail off as fast as N_1^G at higher energies. Thus, ΔE_{av}^+ in Table 2 is larger for BE than for the other models. So although α^{BE} is small, the model gives the same P_c result as the G model because the reaction probability is determined by the fraction of the original population transported above energy, E_0.

The P matrix may be partitioned into four parts at the energy E_0 as shown in Eq. (5). For the consideration of energy accommodation coefficient α, the

$$
P = \left(\begin{array}{c|c} P_I & P_{III} \\ \hline P_{II} & P_{IV} \end{array} \right) \tag{5}
$$

transition probability involving states excited below E_0 in the sub-matrix P_I provides the main contribution to the N_1 vector leading to the average energy change of molecules, ΔE_{av}. The population of reacting states is derived from the transition probability to states above E_0, i.e., P_{II}, which

is connected with down-transitions P_{III} by detailed balance. In the VEM method with m = 1, information is gained regarding elements of P_{II} and P_{III}. Little information is obtained about region P_{I}, so that the models that fit P_c are inadequate to predict α values. This situation is modified for m > 1 where more information can be extracted concerning region I, but with less ability to discriminate between the models that fit region II. Obviously, α and P_c measurements are complementary for the elucidation of the most appropriate analytical forms. Draper and Rosenblatt measured vibrational energy accommodation coefficients of hydrocarbon on a "dirty" metal surface at room temperature by a vibrating diaphragm technique.[2] Although those experiments are not directly comparable to ours, their values of α_{vib} are 0.7 to 0.9 for normal paraffins $(C_4 - C_8)$. Since the G model provides calculated α values nearly close to unity, this might be considered to be the preferred form here. However, it is evident that no single analytical form so far tested gives optimum fit of the data over the whole range of experimental conditions. The recent measurements of α by Foner and Hudson[2] for butane on Pt at 1000°C support the BE model instead.

An important difference exists between weak collider and strong collider behavior in a m = 1 system. For a strong collider, activation to the levels above E_0 occurs mainly from the bulk of the thermal distribution at T_c. Only for weak colliders does the contribution come mainly from the sparsely populated levels just below E_0. This is illustrated in Fig. 5 for colliders of different strengths.

The decline in collisional efficiency that occurs with rise of T_r, at constant T_c in (Table 1) has been observed in the previous cyclobutene VEM studies. The gas-surface interaction approaches strong-collider behavior at T_r < 450 K. This trend appears to be related to the fact that as T_r is lowered, the time that the molecule spends trapped in the gas-surface potential well increases.[11,13]

Table 1. Experimental reaction probability and collisional efficiency
in the $m = 1$ cyclobutene system.

$T_r \backslash T_c$(K)		273	400	500	600
900	$P_c \times 10^4$	1.48	1.54	2.50	6.50
	$\beta_1{}^a$	0.013	0.013	0.022	0.056
800	$P_c \times 10^5$	4.18	4.40	8.50	24.8
	β_1	0.019	0.020	0.039	0.113
700	$P_c \times 10^6$	9.42	10.8	20.5	
	β_1	0.044	0.051	0.096	
600	$P_c \times 10^7$	9.33	11.3	23.5	
	β_1	0.123	0.149	0.310	

a) The collisional efficiency β_1 is defined as $\beta_1 = P_c(T_r, T_c)/P_c^{SC}(T_r)$,
where $P_c^{SC}(T_r)$ is the reaction probability due to a strong collider.
It is the analog of the conventional homogeneous unimolecular
collision efficiency, β .

Table 2. Energy transfer parameters (cm^{-1}) for various
models in the $m = 1$ cyclobutene system.

T_r	Model	$\langle\Delta E\rangle$ or ΔE_{mp} [a]	$\langle\Delta E'\rangle_{E_0}$	$(\Delta E^\dagger_{av})_{E_f>E_0}$ [c]
900		2450	2270[d]	840
800	E	3260	2780[d]	770
700		4080	3120[d]	660
600		-- [b]	--	--
900		3380	3740[e]	420
800	G	3700	4090[e]	440
700		4200	4590[e]	450
600		5630	5640	480
900		1470	2850	1110
800	BE	1340	3490	950
700		1200	4450	780
600		1150	6290	610
900		2880	4390	380
800	BG	2850	4900	360
700		3110	6070	400
600		3290	7300	410

a) For G and BG models, the calculations were made with the standard
deviation set at $\sigma = 0.7 \Delta E_{mp}$.

b) Least square fit was impossible for any physically sensible $\langle\Delta E\rangle$ value.

c) $(\Delta E^\dagger_{av})_{E_f>E_0} = (\bar{E}_f - E_0)_{E_f>E_0}$; values given for case $T_c = 400$ K.

d) Differ from column 3 due to truncation effects approaching $E = 0$ where
the transition probabilities were constrained not to exceed Boltzmann.

e) Differ from column 3 due to truncation near $E = E_0$ as well as $E = 0$. (See (d)).

Table 3. Average energy transfer, ΔE_{av} (cm^{-1}), and vibrational accommodation coefficients, α^a, in the m = 1 cyclobutene system.

$$T_c(K)$$

T_r (K)	Model	273		400		500		600	
900		3850	0.87	$3400(420)^b$	0.86	2880	0.84	2230	0.82
800	G	3200	0.94	2730(440)	0.92	2170	0.90	1500	0.87
700		2420	0.97	1940(450)	0.95	1380	0.92	720	0.89
600		1620	0.96	1150(480)	0.93	620	0.90		
900		770	0.17	740(1110)	0.19	690	0.20	590	0.21
800	BE	690	0.20	650(950)	0.22	560	0.23	430	0.25
700		610	0.24	530(780)	0.26	420	0.28	240	0.30
600		560	0.33	430(610)	0.35	260	0.37		

a) $\Delta E_{av} = \bar{E}_f - \bar{E}_c$; $\alpha = \Delta E_{av}/(\bar{E}_r - \bar{E}_c)$

b) Values of $(\Delta E_{av}^\dagger)_{E_f > E_0}$ in parenthesis from Table 2 shown for comparison.

Table 4. Average thermal vibrational energy $\bar{E}$ of cyclobutene molecules.

T(K)	273	400	500	600	700	800	900
$\bar{E}(cm^{-1})$	290	755	1300	1985	2790	3710	4725

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Figure Captions

Fig. 1 Observed rate constants for cyclobutene isomerization to

1,3 butadiene: the open symbols are for the total

activation reaction, $k_t(T_r,T_c)$, and the closed circles are for

the reservoir wall reaction, $k_c(T_c)$. The X's represent data

which was dropped for reason of the large correction on $k_t(T_r,T_c)$

due to $k_c(T_c)$.

Fig. 2 Relative reaction probability per collision on the basis $P_c(T_r,273) = 1$.

Fig. 3 Results of the least square fit to the experimental P_c curve for each

finger surface temperature: experimental curve (———); E (— -- —);

G (— - —); BE (-----); and BG (— —). The E curve could not fit

the data for $T_r = 600$ K and is not shown.

Fig. 4 Vibrational energy population of cyclobutene for the reaction con-

dition (900, 400). N_r^{eq} and N_c^{eq} are the thermally equilibrated

Boltzmann populations at the temperatures T_r and T_c, respectively.

$k(E)$ is the isomerization rate constant calculated by RRKM theory.

BE and G represent the N_1 population after one collision, calculated

from the least square fit with the BE and G models. These normalized

population curves refer to the two left ordinates.

Fig. 5 The relative probability of up-transitions to the N_1 population at

E_0, given by $P_{E_0 \leftarrow i} \, n_{c,i}$, is illustrated for G and BE models with

two sets of values of the parameters, corresponding to strong(er) and

weak(er) collisions. The several sets for the two models give roughly

similar values of P_c. The calculation was made for the condition

$T_r = 900$ K and $T_c = 400$ K; $\langle \Delta E \rangle (cm^{-1})(P_c) = 4000 \, (8.53 \times 10^{-4})$ and

1500(3.44x10^{-9}) for the G model; and 2000 (7.12x10^{-4}) and 500 (2.94x10^{-9}) for the BE model. The ordinate is in arbitrary linear units rather than log units so as to bring out detail. Some irregularity due to quantized nature of the state density is revealed at E < 2000 cm^{-1}.
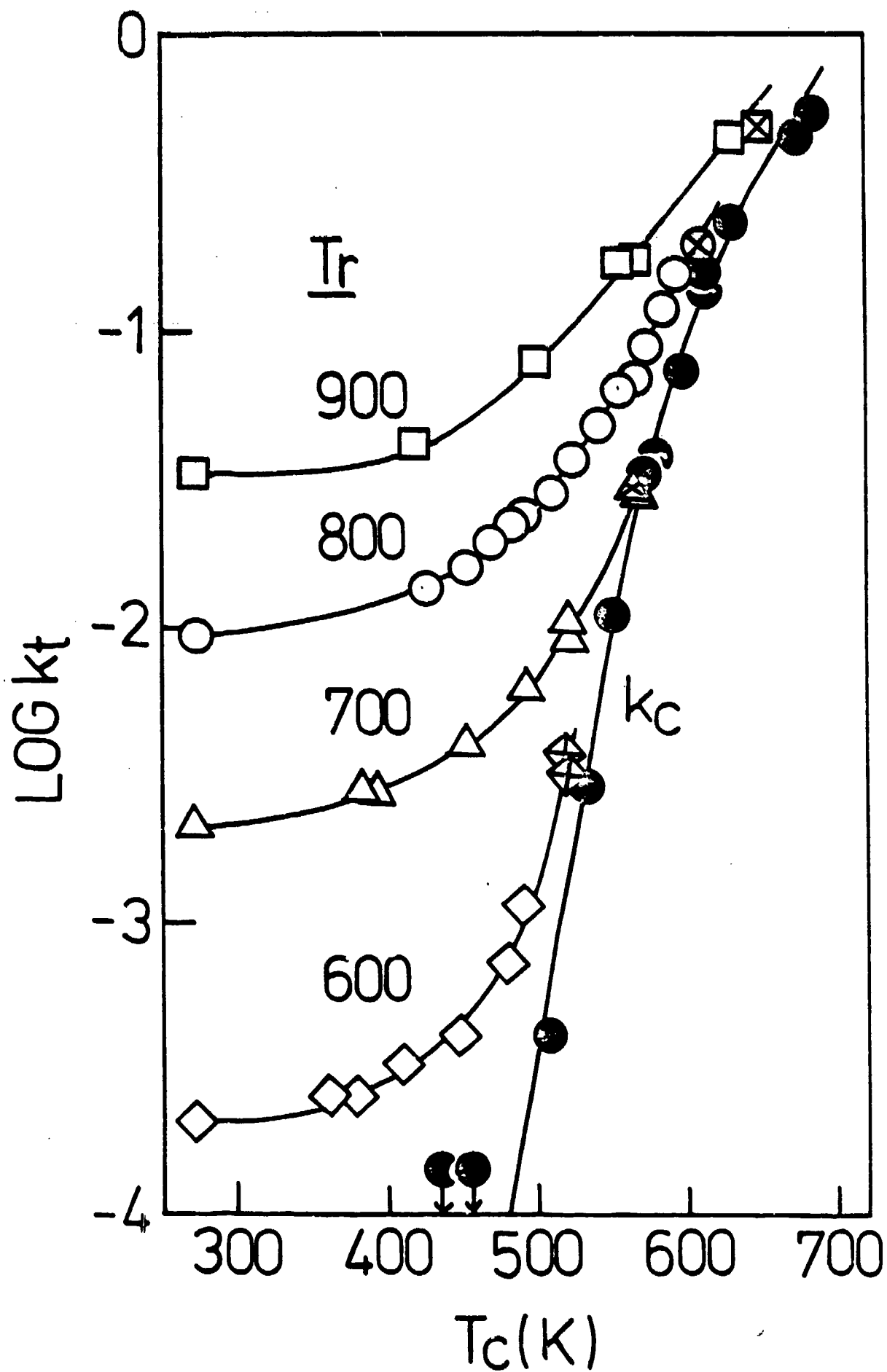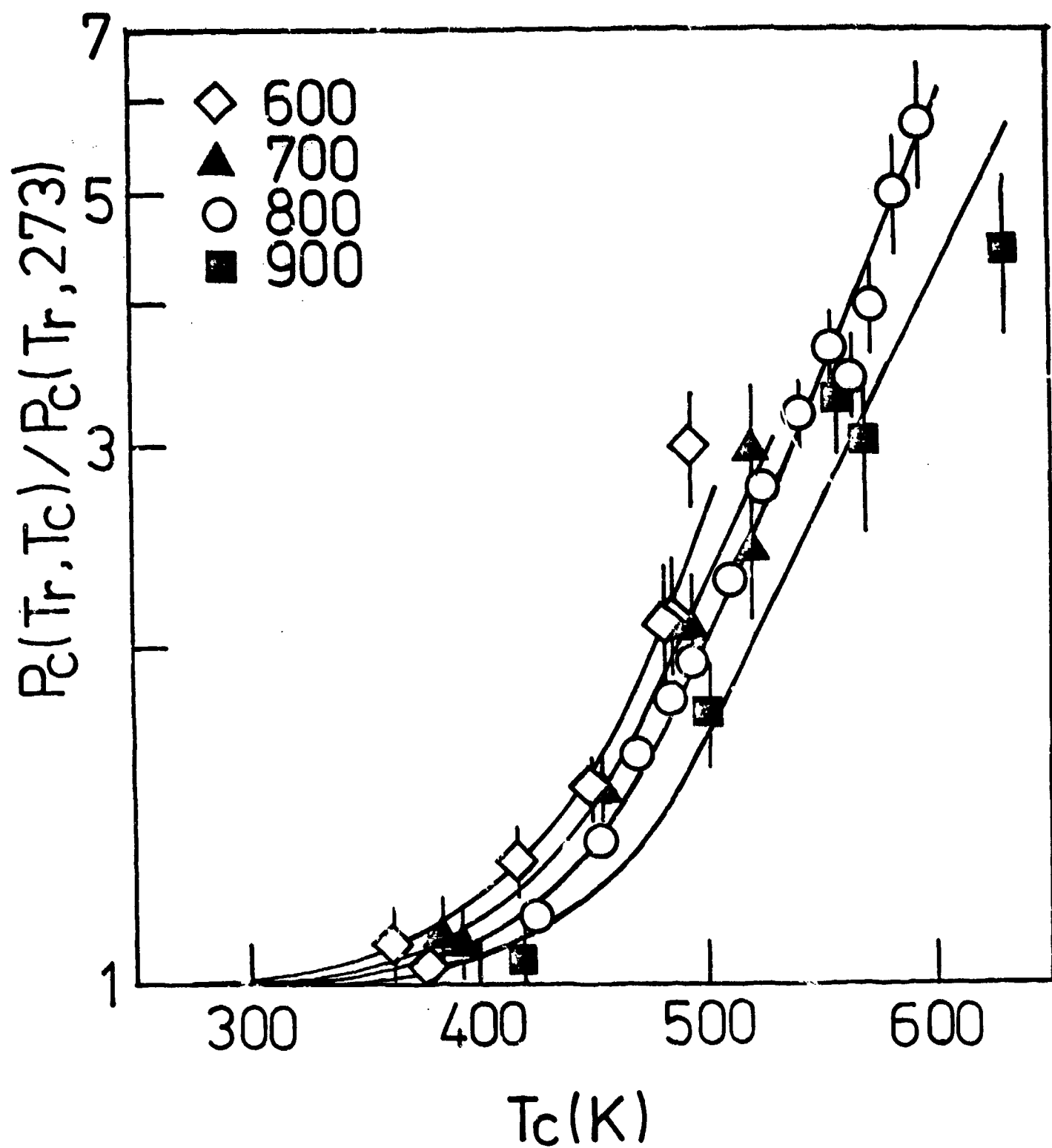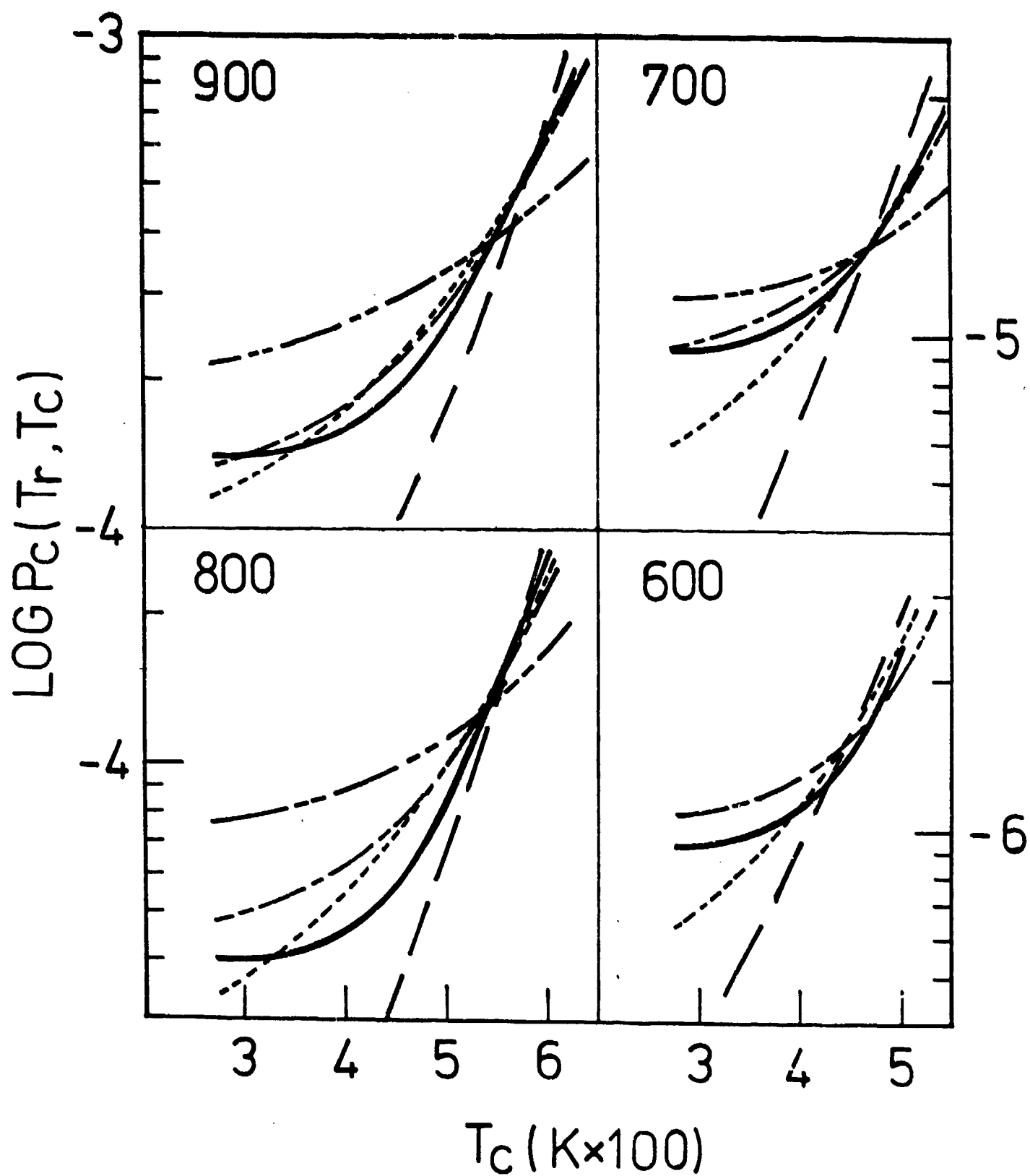
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig 5